

A Rapid Screening Procedure for the Analysis of Radiolytic Organic Vapor Using Solid Phase Microextraction (SPME) and SPME In-Situ Derivatization

A. Alcaraz*, J. S. Haas, R. E. Whipple, P. Grant, and B.D. Andresen
Lawrence Livermore National Laboratory
Livermore, CA 94550

A major effort is currently underway to remediate nuclear production facilities (e.g., Hanford, WA and Savannah River, SC). One of the tasks associated with cleanup efforts is the characterization of radioactive mixed waste, in particular, the headspace volatiles. The vapors produced by stored reprocessing waste (both inorganic and organic) can be toxic and flammable. A variety of traditional analytical methods have been applied to characterize these hazardous gases. However, these methods are time consuming and multi-step procedures (especially when preparing samples for gas chromatography-mass spectrometry (GC-MS) analysis). Results of our recent studies utilizing liquid and headspace SPME, followed by in-situ derivatization, indicate that many of the time-consuming steps necessary to prepare a sample for GC-MS analysis can be eliminated. We have determined that the use of SPME for headspace analysis can facilitate the isolation of organic compounds from highly radiolytic vapor. To demonstrate this, solutions of tributylphosphate (TBP), dodecane (and/or kerosene), and 3.0 M nitric acid were irradiated with a ^{60}Co source at integrated exposure of approximately 50MR and 70MR. These test samples modeled the PUREX process. The multicomponent solutions were analyzed for radiolytic organic products using conventional headspace sampling (gas tight syringes) and SPME, followed by GC-MS analysis. The headspace syringe sampling and SPME results were compared. The liquid organic phase, and aqueous phases of different PUREX solvent systems were also analyzed. In each irradiated dodecane and/or kerosene system, several C4 to C7 alkanes, alkenes, and aldehydes have been identified. Four types of SPME fibers were evaluated: 100(m polydimethylsiloxane, 85(m polyacrylate, 65(m polydimethylsiloxane/divinylbenzene, and 65(m carbowax/divinylbenzene coatings (Supelco). Samples were then analyzed directly by GC/MS (Varian Saturn IV). Data will be presented showing the comparison of conventional headspace analysis vs. SPME headspace for radiolytic vapor sample collection.

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract W-7405-ENG-48.